⑫ # EUROPEAN PATENT APPLICATION

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㊴ **Method of synthesizing hydrocarbons and alcohols.**

㊗ Improved economies are achieved in the synthesis of hydrocarbons and alcohols from hydrogen/carbon monoxide mixtures by adding steam to a hydrogen-lean synthesis gas derived, e.g., from the gasification of a liquid or solid fossil fuel and carrying out the synthesis in the presence of a catalyst comprising hydrided titanium supported on a metal or intermetallic compound capable of forming an unstable hydride.

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METHOD OF SYNTHESIZING HYDROCARBONS AND ALCOHOLS

This invention relates generally to the production
of hydrocarbons and alcohols from mixtures of hydrogen and
carbon monoxide, especially mixtures largely composed of
hydrogen and carbon monoxide that are derived from the gasi-
5 fication of liquid and solid fuels, and more particularly,
to the use of steam to improve the economy of such a process.

Background of the Invention

Prior art methods for the production of hydrocarbons
such as methane and ethane have employed carbon monoxide and
10 hydrogen over nickel catalysts of various types. The cost of
nickel catalyst is quite high, both because of raw material costs
and because of difficulties experienced in the manufacturing
process, the latter requiring that the nickel be supported
on some type of inert base. Moreover, the attrition of nickel
15 catalyst is high because the processes that have been used re-
quire relatively high temperatures which in turn causes a
sintering type of breakdown that rapidly decreases the activity
of the catalyst as a function of time.

Nickel catalysts are also sensitive to poisoning by
20 a number of impurities usually found in the hydrogen and carbon
oxide reactants. For example, hydrogen sulfide has been found
to poison nickel catalysts even in very small concentrations by
forming nickel sulfide. The thermodynamics of the system is
such that sulfur poisoning can be reversed by raising the tempera-
25 ture or increasing the hydrogen to hydrogen sulfide ratio in
the feed or both. However, the use of higher operating
temperatures with nickel catalysts is restricted by a sintering
problem. Also the purity of the feed gas is inherently limited
as a practical matter by the costs of purification.

The reaction of carbon monoxide with hydrogen in the presence of nickel catalyst requires temperatures in the range of 300° to 500°C. to produce significant reaction rates. Temperatures within this range cause relatively rapid deterioration of the nickel catalyst. In addition, very little ethane can be produced with nickel catalysts since the ethane reaction is favored only at lower temperatures. Furthermore, practically no alcohol formation is observed over nickel catalysts. In general, the formation of alcohols is believed to follow a mechanism different from that prevailing in the synthesis of hydrocarbons. Heretofore a different catalyst, namely, zinc oxide, was required for the synthesis of methanol.

A further problem restricting the use of prior art catalysts is carbonyl formation. The carbonyls of metals like nickel, ruthenium and iron are extremely toxic compounds. They also have very low boiling temperatures and thus would be present in a vapor phase at the temperatures required for the synthesis of methane, ethane and higher carbon compounds. Carbonyl formation causes depletion of the catalyst as well as posing a severe health and safety problem. Such problems with prior art catalysts can be avoided only by carefully controlling the operating temperature, pressure, carbon oxide to hydrogen ratio and other operation parameters and conditions.

Even at the elevated temperatures indicated, the reaction rates with nickel and other known catalysts are relatively slow and require a high residence time in the reactor vessel, which in turn results in a relatively slow production rate for the final product desired.

In my prior patent 4,139,551, a process is disclosed
for producing methane and ethane from hydrogen and oxides of
carbon that avoids a number of the foregoing disadvantages.
In this prior process methane and ethane are produced from
5 mixtures of hydrogen and one or more oxides of carbon by
passing the mixture over an iron/titanium catalyst wherein
the atomic ratio of titanium to iron is preferably about 1.1:1.
By using the iron/titanium catalyst, lower temperatures and
pressures can be used that are required with the nickel
10 catalyst and the formation of toxic carbonyl compounds is
avoided. Also higher reaction rates can be achieved.

While the process disclosed in U. S. patent 4,139,551
provides a number of important advantages over prior art processes
using nickel catalysts, it still leaves something to be desired
15 in cases where the starting material used is derived from the
gasification of any of various fossil fuel sources, especially
coal. Gaseous mixtures thus produced tend to contain carbon
monoxide and hydrogen in proportions such that there is insuffi-
cient hydrogen to form the desired hydrocarbons. Thus, if such
20 starting mixtures are used, additional hydrogen must be incor-
porated in the mixtures and such additional hydrogen is quite
expensive.

Objects of the Invention

It is a general object of the invention to provide
25 a novel and improved process for the manufacture of hydrocarbons
and alcohols from oxides of carbon and hydrogen. It is another
object of the invention to manufacture hydrocarbons using less
expensive raw materials. It is still another object of the
invention to provide a process for the co-production of hydrocarbons

and alcohols. It is a further object of the invention to provide
a process for making hydrocarbons from a hydrogen-lean gasifica-
tion product obtained from the gasification of coal and similar
substances, e.g., a product obtained from the underground gasi-

5   fication of coal. It is a still further object of the invention
to increase the heating value of a gas initially obtained from
gasification of coal, residua, oil shale, tar sands and similar
carbonaceous substances by converting the carbon monoxide present
in such a gas to methane, ethane and higher hydrocarbons as well

10 as alcohols. It is a still further object of the invention to
provide a commercially feasible process for co-production of
substitute natural gas, LPG, gasoline, liquid hydrocarbons,
and alcohols that can be mixed with gasoline in an integrated
plant from a feed obtained by the gasification of coal, residua,

15 oil shale, tar sands and similar carbonaceous materials through
the use of known gasification technology. Other objects of the
invention will be in part obvious and in part pointed out
hereafter.

Summary of the Invention

20   The present invention is based on the finding that
by incorporating water vapor, usually in the form of steam,
into a synthesis gas of the type disclosed in my patent number
4,139,551 and by using a catalyst of the type described below,
it is possible to employ as a starting material a synthesis

25 gas that is quite lean in respect to elemental hydrogen and still
achieve a good yield and the other advantages attained when using
the patented process. In accordance with the present process
a product of the gasification of e.g. coal is used that contains

a stoichiometric deficiency of the hydrogen required for
formation of hydrocarbons and the deficiency is made up
by the hydrogen content of the added steam.

5 While we do not wish to be bound as to any particular
mechanism of the reaction that occurs, it appears probable that
the reaction proceeds in accordance with mechanism I or mechanism II
given below or perhaps in accordance with both mechanisms.

Mechanism I

One possible mechanism involves a shift conversion
10 followed by a synthesis as follows:

The reaction between carbon monoxide and water repre-
sented by the equation:

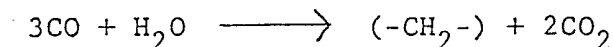$$CO + H_2O \longrightarrow CO_2 + H_2$$
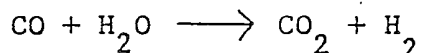
is known as the water gas shift conversion and produces elemental
15 hydrogen which, as a component of the feed, can react with carbon
monoxide to form hydrocarbons and alcohols as follows:

$$xCO + 2 x H_2 \longrightarrow (-CH_2-)_x + x H_2O$$
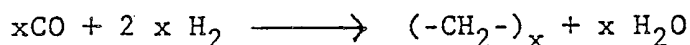
Mechanism II

A second possible mechanism is illustrated by the
20 following equation:

$$3CO + H_2O \longrightarrow (-CH_2-) + 2CO_2$$

The foregoing equation represents the so-called
Kolbel-Engelhardt synthesis which is known to produce hydro-
carbons. However, the catalysts previously proposed for this
25 reaction have had activities so low as to make the process

unattractive commercially. The catalysts of the present inven-
tion, when prepared as described hereafter, exhibit substantially
improved activity in this reaction.

The objects and advantages of the present invention
5   are achieved in general by contacting steam and carbon monoxide
in a hydrogen atmosphere and in synthesis proportions under
synthesis conditions to form hydrocarbons and alcohols using
a catalyst comprising hydrided titanium supported on a metal
or inter-metallic compound capable of forming unstable hydrides,
10   more particularly, hydrides that are unstable at a temperature
within the range of atmospheric temperature to about 100°C.
As pointed out more fully below, before being used in the synthesis
process, the catalyst is desirably activated by alternate hydriding
and dehydriding steps to cause a partial physical disintegration
15   of the catalyst and thereby increase its surface area. The
hydrogen atmosphere that is necessary for maintaining the catalytic
activity may be provided by adding hydrogen to the feed mixture
of steam and carbon.monoxide. As pointed out hereafter, the
amount of added hydrogen may vary over a wide range.

20   The catalysts of this invention for the first time
permit the use of a steam/carbon monoxide feed to achieve
commercially feasible hydrocarbon production rates. The cost
of the feed stock is significantly reduced by substituting
the relatively inexpensive steam for costly hydrogen. The
25   catalysts of this invention make it possible to use hydrogen-lean
synthesis gases produced, for example, by conventional gasifi-
cation processes directly, i.e., without the need for an addi-
tional water gas shift step, in the syntheses of hydrocarbons
and alcohols. Consequently, the cost of production of hydrocar-
30   bons and alcohols is substantially lowered. The catalysts of

the invention also for the first time permit the use of signi-
ficantly lower operating temperatures and pressures in achiev-
ing commercially feasible production rates in the synthesis
of alcohols. As the thermodynamics of the chemical system con-
5 cerned permits higher equilibrium conversion at lower tempera-
tures, the actual yields are greatly improved. Furthermore,
again with respect to the alcohol synthesis, equipment require-
ments are much less stringent and less costly by reason of the
lower operating pressures that can be employed at the process
10 temperature selected. In addition, the use of the catalyst and
the process of this invention greatly improves the economics of
synthetic production of hydrocarbons and alcohols, which are
valuable fuels and starting materials of many organic syntheses,
by allowing the co-production of the same in an integral chemical
15 complex which will produce the feed for the said synthesis
through a more economical gasification process than heretofore
possible,as well as employing a more economical process in the
actual synthesis of hydrocarbons and alcohols.

The catalyst of this invention is free from many
20 problems commonly encountered with prior art catalysts.
For instance, there is little risk of carbonyl formation and
also much less poisoning or deactivation of the catalyst through
the smothering of adsorbing sites by the adsorption of impuri-
ties that normally exist in commercially available carbon
25 monoxide. To the contrary, it has been found that the catalytic
activity of the catalyst employed in the present invention
increases with aging in an atmosphere containing hydrogen.

This enhancement of activity is the result of cracks and
fissures formed in the catalyst particles, both microscopically
(surface cracks) and macroscopically (breakage into smaller
particles), with the attendant increase in the active surface
5   area of the catalyst. Moreover, continuous cleaning of the
catalyst surface from impurities by the hydrogen present in
the reaction atmosphere prolongs the activity of the catalyst.

General Description of Preferred Embodiment

As indicated above, the present catalysts comprise
10   a titanium hydride and a support which may be either a metal
or inter-metallic compound capable of forming unstable hydrides.
As will be pointed out below, a wide variety of metals may be
used as the supporting metal or in the supporting inter-metallic
compound of the catalyst. However, the preferred support is an
15   inter-metallic compound of iron and titanium.

The Fe/Ti alloy used in preparing the catalyst may
be considered as comprising two phases, namely, (a) free titanium
metal capable of being hydrided upon proper exposure to a hydrogen
atmosphere and (b) an inter-metallic compound of iron and titanium
20   in a 1:1 ratio that forms the support for the titanium metal, and
after hydrogenation, for the titanium hydride. The support or
carrier of phase (b) may be a commercially available alloy
having the desired 1:1 ratio obtainable, for example, from the
International Nickel Company. This alloy is further described
25   in a book entitled "Constitution of Binary Alloys", First Supple-
ment, by R. P. Elliott, published by McGraw Hill, New York, N. Y.,
1965 and a paper of Reilly et al. referenced more fully below.

The carrier alloy is formed from relatively pure iron and
titanium by a melting process requiring temperatures in the
range of 1500° to 1900°C. Although the carrier can be made
from commercial grade iron, the purity of electrolytic iron
5   is preferred.

The supported catalyst comprising a separate
titanium phase A may be made in the same way as the binary
1:1 alloy, since an alloyed mixture containing more than
1 mole of titanium for each mole of iron will produce a compo-
10   sition consisting of two phases, namely, the inter-metallic
compound having a titanium to iron mole ratio of approximately
1:1 and pure titanium, the latter being converted to hydrided
titanium in a hydriding step. The titanium hydride formed
in this step is a non-stoichiometric hydride which contains
15   slightly less hydrogen than the stoichiometric dihydride
and may, for example, have the approximate formula $TiH_{1.98}$.
This titanium hydride is a relatively stable compound which
remains as such throughout the production process and is
continually activated (decontaminated) as long as it is
20   in contact with significant amounts of hydrogen in the
synthesis process.

Although hydrided titanium appears to exhibit increased catalytic activity when alloyed with or otherwise supported on the iron-titanium bi-metallic compound, the catalytically active component is considered to be the hydrided titanium.

5 For further information on the independent properties of each of these compounds, particular reference is made to the article entitled "Formation and Properties of Iron Titanium Hydride" by J. J. Reilly and R. H. Wiswall, Jr., of Brookhaven National Laboratory, published in Inorganic Chemistry, Vol. 13, No. 1,

10 1974, at pages 218-222, and to the book by W. M. Mueller, et al., entitled Metal Hydrides as published by Academic Press, New York, N. Y., 1968.

The preparation of the hydrided catalyst and its activation will now be described.

15 Activation Procedure

The titanium/iron alloy used in preparing the preferred catalyst of the invention is usually received from the manufacturer in granular form. The granular material as received is coated with an oxide layer and in this state neither the titanium

20 phase (a) nor the inter-metallic phase (b) can form a hydride. Also the granules have other surface and internal impurities such as carbon and nitrogen compounds and adsorbed gases other than hydrogen and nitrogen. Initial cleaning of the particles and formation of the catalyst containing the titanium in

25 hydrided form is desirably accomplished by charging the granular material as received into a sutiable reactor and subjecting it to hydrogen gas, preferably at temperatures in the range of 200°C. to 400°C. and at pressures in the range of 0 to 3000 p.s.i.g., preferably 150 to 200 p.s.i.g., for an extended period

30. of time.

This initial exposure to hydrogen is followed by
an outgassing step and then alternate pressurizing of the
catalyst bed with hydrogen and outgassing so that phase (b) of
the catalyst is successively hydrided and dehydrided. This

5   process breaks up the catalyst granules into smaller particles
and also produces multiple cracks in the surface of each indivi-
dual granule, thereby greatly increasing the reactive surface
area of the catalyst bed. The dehydriding step may be carried
out at a temperature and hydrogen partial pressure that favors

10 the decomposition of the hydride of phase (b) as determined by
the theremodynamic equilibrium diagram of the inter-metallic
compounds used. However, it is preferably carried out at or
about 200°C. by drawing a slight vacuum of one or two inches
of water on the reactor vessel containing the catalyst bed.

15 Although the dehydriding may also be carried out by purging
the reactor vessel with an inert gas such as helium, extreme
care must be observed under such circumstances for the commercial
grades of inert gases such as helium also contain oxygen at an
impurity level which permanently poisons the catalyst by forming

20 a stable oxide upon contact therewith at elevated temperatures.
The hydriding step may be carried out at a temperature
and pressure that favors the formation of the hydride phase (b)
as determined from the equilibrium conditions. of the material
used. Hydriding is preferably carried out at a temperature of

25 20° to 25°C. and at a pressure of the order of 1,000 psia.
Any commercially available grade of hydrogen gas may
be used in the activation process. However, the use of relatively

high purity hydrogen permits the attainment of acceptable

activation in a fewer number of cycles. Whether a less

expensive grade of hydrogen or faster activation of the

catalyst is desirable from the point of view of process

5 economics, will depend upon the conditions at a given

manufacturing plant.

If the hydrogen gas used in the activation process

is less than 99.999% pure, then a high temperature hydrogen

treatment step between the dehydriding and hydriding steps

10 should be incorporated in the activation cycle. This added

step is essentially the same as the initial hydrogen treatment

and in this case removes the gases such as the impurities in

the hydrogen gas used that become adsorbed on the catalyst

particles during the hydriding step. Therefore, following

15 the dehydriding step the reactor is filled with hydrogen gas

at a temperature of about 200° to 400°C. and a pressure of

approximately 150 to 200 psia preferably for four to six hours.

Following this high temperature hydrogen treatment the hydrogen

gas is again evacuated from the reactor by drawing a vacuum

20 and the catalyst bed is cooled to 20° to 25°C. Upon reaching

this temperature level, the reactor is pressurized with hydrogen

gas at about 1000 psia and kept at these conditions until

phase (b) is completely hydrided. The extent to which the

hydriding reaction has proceeded may be followed by monitoring

25 either temperature or pressure changes in the reactor and noting

the time at which these parameters return to their initial

values. Alternatively, the hydriding can be continued for a

specific period of time, e.g., one-half hour.

After the hydriding reaction is completed the hydrogen
is drawn off from the reactor by applying a vacuum until the
pressure in the reactor is approximately one to two inches
of water and concurrently the catalyst bed is heated to 200°C.
5   in order to dehydride phase (b). The foregoing hydriding-
dehydriding cycle is carried out until phase (b) of the catalyst
is capable of being hydrided and dehydrided very rapidly. In
the case of catalyst compositions that are to be prepared in
powdered form, the hydriding and dehydriding cycles are continued
10   until the desired particle size is attained.

Synthesis Process

The catalyst prepared as described above is charged
to a suitable reactor and a gaseous feed stream comprised of
hydrogen, carbon monoxide and water vapor is continuously
15   passed over the catalyst bed in the reactor at a suitable
temperature and pressure. The range of synthesis temperatures
is governed by two counteracting factors. On the one hand,
higher temperatures result in high reaction rates. On the
other hand, the hydrogen concentration at the equilibrium
20   of the water gas shift reaction is favored by lower temperatures.
The practical temperature range appears to be about 150°C. to
350°C.

Higher pressures favor both the rate of production
of the desired products and the equilibrium concentrations of
25   these products. The reaction may be carried out at a pressure
within the range 1 to 200 atmospheres. The preferred range
appears to be 30 to 100 atmospheres.

As indicated above, the feed stream for the process
may be obtained by the gasification of coal, residua, oil
shale or tar sands by any of the well known gasification
techniques. The technology used will vary according to the
5   nature of the material to be gasified. The gasification product
is then mixed with steam and in some cases hydrogen at selected
ratios and fed to the reactor that contains the catalyst.
A substantial proportion of the hydrogen is incorporated
in the feed mixture to enhance the reaction of water vapor
10 and carbon monoxide rather than to enter into the reaction
itself. Therefore, hydrogen is separated from the product
stream and continuously recycled. However, the hydrogen may
be gradually consumed to a relatively small extent by reaction
with carbon monoxide and/or carbon dioxide. In that case a
15 replenishment of the hydrogen so consumed is necessary and this
may be accomplished for instance either by increasing the
steam/carbon monoxide ratio or by adding hydrogen to the
system.

In the production of the synthesis gas, the water/gas
20 shift step which is ordinarily carried out subsequent to the
gasification process to adjust the hydrogen/carbon monoxide
ratio or to generate hydrogen may be omitted when the catalyst
and process of the present invention is used. Alternatively,
a small proportion of the gasification product may be subjected
25 to the shift reaction. Since hydrogen is effectively produced
during the synthesis process, significant cross-reductions are
achieved.

The amount of added hydrogen will depend to some extent
on the hydrogen content of the synthesis gas. As indicated
30 above, the proportion of hydrogen in the feed mixture can vary

over a wide range, i.e., from a molar ratio of hydrogen to steam/carbon monoxide mixture of about 1:9 to 99:1. The minimum amount of hydrogen is about 10 volume %.

The ratio of CO to steam does not appear to be parti-
5 cularly critical and may be varied over a relatively wide range depending on the product or products to be produced. In most cases this ratio should desirably be greater than 1.5:1.

Other Embodiments of the Invention

Although a single embodiment of the present invention
10 has been described, other useful embodiments and variations of the catalyst composition, the mode of preparation and treatment of the catalyst and synthesis steps will be apparent to those skilled in the art. As indicated above, the catalyst may broadly comprise a hydrided metal and a support comprising a metal or
15 inter-metallic compound characterized by the fact that it is capable of forming an unstable hydride. The hydrided metal may be hydrided titanium as described in detail above, or alternatively hydrided zirconium. Of the elemental metals that may be used as a support, vanadium, zirconium, and niobium
20 may be mentioned. A considerable number of inter-metallic compounds may be used, including compounds of titanium with metal selected from the group consisting of iron, nickel, cobalt, chromium, molybdenum and manganese. Among the specific inter-metallic compounds that may be mentioned are those of the follow-
25 ing formulas: $FeTi$, $NiTi_2$, $TiCo$, $TiCr_2$, $ZrNi_2$, $ZrMo_2$, $ZrFe_2$, $ZrCo_2$, $ZrMn_2$, $TiFe_{0.8}Mn_{0.2}$, $TiFe_{0.9}V_{0.1}$, $TiFe_{0.8}Cr_{0.2}$, $TiFe_{0.8}Mo_{0.2}$, $TiCo_{0.8}Mn_{0.2}$, $TiCo_{0.9}Fe_{0.1}$, $TiCo_{0.8}V_{0.2}$, $TiCo_{0.9}Ni_{0.1}$, $TiCo_{0.8}V_{0.2}$, $TiCo_{0.9}Ni_{0.1}$, $TiCr_{1.8}Fe_{0.2}$, $TiCr_{1.8}V_{0.2}$, $TiCr_{1.7}Mo_{0.3}$, VTi_2, $NiTi_3$, $CoTi_2$, and $CrTi$.

Other examples of inter-metallic compounds capable of forming hydrides that are unstable at temperatures up to 100°C. can be found in the literature.

Other variations within the scope of the invention

5　involve combining titanium dihydride with catalytically active metals for this reaction such as ruthenium and palladium either in the form of mixtures of multi-component (e.g. ternary, quaternary or higher) alloys, or supporting this catalyst upon other inter-metallic compounds or on an inert carrier material

10　or other substrates.

By way of further example, activation of the catalyst can be achieved, although at a slower rate, by exposing the catalyst to hydrogen in the feed stream of the synthesis process itself, particularly, if the product stream is recycled until

15　a desired product concentration is achieved. It is therefore to be understood that the foregoing specification is not intended to be limited to the preferred embodiment of the invention described and that other embodiments are contemplated within the scope of the appended claims.

1.   A method of making hydrocarbons and alcohols
which comprises contacting a gaseous mixture of steam,
hydrogen and carbon monoxide in synthesis proportions at
synthesis conditions with a catalyst comprising hydrided
titanium supported on a metal or inter-metallic compound
capable of forming an unstable hydride.

2.   A method of making hydrocarbons and alcohols
which comprises contacting a gaseous mixture of steam,
hydrogen and carbon monoxide in synthesis proportions at
synthesis conditions with a catalyst comprising hydrided
titanium supported on a metal or inter-metallic compound
capable of forming hydrides that are unstable at atmospheric
temperature.

3.   A method of making hydrocarbons and alcohols
which comprises contacting a gaseous mixture of steam, hydrogen
and carbon monoxide in synthesis proportions at synthesis
conditions with a catalyst comprising hydrided titanium supported
on an inter-metallic compound capable of forming an unstable
hydride.

4.   A method according to claim 3 wherein said catalyst
is made by preparing a composition comprising free titanium and
said inter-metallic compound and exposing said composition to
hydrogen at an elevated temperature to convert free titanium
thereof to hydrided titanium.

5.   A method according to claim 4 wherein said
catalyst is activated by alternately hydriding it at ambient
temperature and dehydriding it at an elevated temperature to
increase the surface area of said catalyst.

6. A method according to claim 5 wherein said catalyst is hydrided at a pressure above atmospheric and dehydrided at a pressure below atmospheric..

7. A method according to claim 3 wherein the volumetric ratio of hydrogen to steam and carbon monoxide in said gaseous mixture is from about 1:9 to 99:1.

8. A method according to claim 3 wherein the inter-metallic compound is a compound of titanium or zirconium with a metal selected from the group consisting of iron, nickel, cobalt, chromium, molybdenum and manganese.

9. A method according to claim 8 wherein the inter-metallic compound is a compound of titanium and iron.

10. A method according to claim 9 wherein the molar ratio of titanium to iron in the inter-metallic compound is about 1:1.

11. A method of making hydrocarbons and alcohols which comprises contacting a gaseous mixture of steam, hydrogen and carbon monoxide in synthesis proportions at synthesis conditions with a catalyst prepared by alloying titanium with a second metal capable of forming an inter-metallic compound with titanium under alloying conditions such as to produce an inter-metallic compound of titanium and said second metal as well as free titanium in an amount effective when hydrided to catalyze the conversion of steam, hydrogen and carbon monoxide to hydrocarbons and alcohols and then exposing the alloy of said second metal and titanium to hydrogen under hydriding conditions such as to hydride at least a portion of said free titanium.

12. A method according to claim 11 in which said second metal is selected from iron, nickel, cobalt, chromium, molybdenum and manganese.

13. A method according to claim 11 wherein said hydriding conditions are such as to remove oxides from the surface of said alloy.

14. A method according to claim 11 wherein said inter-metallic compound is a compound of titanium and iron.

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	DOCUMENTS CONSIDERED TO·BE RELEVANT		**CLASSIFICATION OF THE APPLICATION (Int. Cl.³)**
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	FR - A1 - 2 266 676 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) * claims 1, 5 *	1	C 07 C 1/22 C 07 C 29/15 B 01 J 31/38
A D	FR - A1 - 2 380 239 (RAFEL INDUSTRIAL GROUP) * claims 1, 8 * & US - A - 4 139 551	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.³)
			B 01 J 31/02 B 01 J 31/26 B 01 J 31/38 C 07 C 1/20 C 07 C 1/22 C 07 C 29/15

X	The present search report has been drawn up for all claims	
Place of search Berlin	Date of completion of the search 03-06-1981	Examiner KNAACK

EPO Form 1503.1   06.78